PITTING CORROSION BEHAVIOUR OF ALUMINIUM ALLOYS

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ABSTRACT

The present work is aimed to investigate the effect of temperature and concentration of solution on the pitting corrosion of AA6061 – T6 aluminium alloy and study its electrochemical behaviour and physical behaviour in sodium chloride (NaCl) solution using the polarization technique. The experiments were carried out under static conditions at different NaCl concentration solutions (3.5, 4.5 and 5.5) wt% and different temperatures (25, 35, 45, 55 and 65) ^{o}C. This experiment started with different NaCl concentration solutions at room temperature condition by using potentiostat/galvometer instrument. Water bath machine had been used to control the solution temperature in this experiment. Natural pitting corrosion experiment had been tested for 2 months in different NaCl concentration solutions. Comparison between two methods which were tested in different concentration was discussed. It was found experimentally that increasing in NaCl concentration and temperatures lead to decrease in the breakdown potential (E_{corr}) and increase in corrosion rate of as-received materials. Based on the results obtained, the corrosion rate increased from 0.1529 mmpy to 0.3650 mmpy for the electrochemical experiment and 0.2517 mmpy to 0.4692 mmpy for natural pitting when concentration of the solutions increased from 3.5 wt% to 5.5 wt%. The influence of solutions' temperature (25 – 65 ^{o}C) on the pitting corrosion of AA6061-T6, showed the changes of the corrosion rate from 0.1529 mmpy to 1.205mmpy. In conclusion, the highest corrosion rate obtained at the highest solution temperature. The increased in concentration and temperature lead to the increasing of corrosion rate of AA6061-T6.

ABSTRAK

Satu eksperimen yang bertujuan mengkaji kesan-kesan beberapa pembolehubah terhadap hakisan bopeng pada AA 6061-T6 aloi aluminium dan mengkaji fizikal elektrokimia dan fizikal dalam larutan batrium kloida (NaCl) dengan menggunakan teknik polarisasi telah dijalankan. Kajian ini telah dijalankan dengan menggunakan pelbagai kepekatan NaCl ((3.5, 4.5, 5.5) wt% dan suhu yang berbeza (25, 35, 45, 55 and 65) ^{o}C. Eksperimen ini bermula dengan larutan yang berbeza kepekatan NaCl pada keadaan suhu bilik. “Water bath” yang boleh mengawal suhu larutan NaCl telah digunakan dalam eksperimen. Terdapat satu eksperimen semulajadi bagi hakisan bopeng telah dikaji dalam dua bulan dengan menggunakan larutan kepekatan NaCl yang berbeza. Perbandingan dua kaedah yang berbeza digunakan untuk menguji kehakisan dalam kepekatan yang berbeza telah dinyatakan. Eksperimen peningkatan dalam kepekatan dan suhu larutan NaCl mengakibatkan penurunan dalam potensi kerosakan (E_{corr}) dan meningkatkan kadar hakisan sampel yang diujikan. Berdasarkan keputusan yang diperolehi, kadar hakisan bagi eksperimen elektrokimia menambah dari 0.1529 mmpy sehingga 0.3650 mmpy. Bagi bopeng semula jadi, kadar hakisan telan meningkat dari 0.2517 mmpy sehingga 0.4692 mmpy semasa kepekatan larutan NaCl meningkat dari 3.5wt% sehingga 5.5wt%. Kadar hakisan menunjukkan perubahan dari 0.1529 mmpy dan meningkat sehingga 1.205 mmpy bagi suhu larutan NaCl yang berbeza (25 – 65) ^{o}C. Kesimpulannya, pada suhu 65^{o}C mendapat kadar hakisan yang paling tinggi. Peningkatan kepekatan dan suhu menyebabkan peningkatan kadar kakisan AA6061-T6.

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LIST OF SYMBOLS

A	Exposed area
d	Density
E	Potential
E_B	Breakdown potential
E_b	Transpassivation potential/ critical pitting potential
E_{corr}	Corrosion potential
E_p	Pitting potential
E_{pp}	Critical passivation potential
E_R	Repassivation potential
$E_{rev,\ O2}$	Reversible potential of the oxygen electrode
i	Current density
I_{corr} / i_c	Corrosion current density
$i_{c,h}$	Final free corrosion current density
i_{pp}	Passivation current density
K	Constant value
r	Pit radius or depth
t	Time
$\%$	Percentage
^oC	Celcius
α	Direct proportional
β_a	Anodic Tafel constant
β_c	Cathodic Tafel conctant

LIST OF ABBREVIATIONS

Al	Aluminium
Al_3^+	Aluminium ion
Al_2O_3	Aluminium Oxide
CPT	Critical pitting temperature
Cl^-	Chloride ion
Cr	Chromium
CR	Corrosion rate
Cu	Copper
e^-	Electron
EW	Equivalent weight
Fe	Iron
H^+	Hydrogen ion
H_2O	Water
i.e.	Id est (means in Latin “that is”)
IR	Infrared radiation
Mn	Manganese
mmpy	Milimeter per year
mpy	Mils per year
M.V.	Mean Value
NaCl	Sodium chloride
O_2	Oxygen
OH^-	Hydroxide irons
pH	Power of Hydrogen

P.P.D.	Pits population density
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
Si	Silicon
SIC	Silicon carbide
SS	Stainless steel
Ti	Titanium
UMP	University Malaysia Pahang
Wt%	Weight percentage
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

This chapter explains about the background of study, problem statement, objectives and the scopes of this study. The main purpose for this study can be identified by referring at the problem statement of this study. Furthermore, the details of this study and outcome can be achieved on the objectives and its scopes.

1.2 BACKGROUND OF STUDY

Corrosion can be defined as degradation of a material's properties because of chemical reaction between the components of the material with their environments (Shaw and Kelly, 2006). Appearance of corrosion not only created variety of problems for daily life, but it also has a huge economic and environmental impact on virtually all facets of the world's infrastructure, from highways, bridges, and buildings to oil and gas, chemical processing, and water and wastewater systems (Günter, 2009).

The Electrochemical Society Interface states that aluminium alloys are the largest proportions of nonferrous alloys that are widely used in industrial applications, especially for construction and equipment, containers and packaging, production of automotive, aviation, aerospace, household appliances electronics, food industry, and majority of commercial marine applications. Aluminium and its alloys are characterized by a relatively good electrical and thermal conductivities, low density (2.71 g/cm^3), high ductility and high corrosion resistance. There have several parameters affect the behaviour of aluminium alloys in aqueous environments. The surface properties of the material, nature environment effect, surrounding temperature, pH and the composition

of the aggressive solution influences the composition and microstructure of aluminium alloys. Moreover, mechanical and heat treatment processes also affect the structure and composition of oxide layer on the material surface, which cause more corrosion resistant.

Due to light weight and excellent machining properties, many ship superstructures and liquid cargo containers are made by aluminium alloys. The 5000 series and 6000 series alloys which demonstrate adequate strength and excellent corrosion resistance are the most popular aluminium alloys for use in corrosive environments such as seawater. AA6061-T6 aluminium alloyed with magnesium and silicon displays high strength, excellent extrudability, reasonable weldability and good corrosion resistance. This alloy finds widespread application in ship building (civil and military) and in the fabrication of tank containers for transporting various liquids, where is often welded during manufacturing process. However, this material tends to corrode in chloride-containing environments and form in pitting corrosion.

The aluminium-rich matrix adjacent to magnesium-silicon intermetallic precipitates or silicon-rich phases in aluminium-silicon-magnesium alloys has been shown to be susceptible to preferential corrosion in NaCl solutions. Coarse intermetallic particles containing aluminium, silicon and magnesium act as nucleation sites for pit formation. The formation of pits, in turn, has a detrimental effect on the fatigue life of 6061 aluminium. The fatigue life of aluminium alloys has been shown to be significantly reduced when tested in a 3.5% NaCl solution compared to the fatigue life of the same alloy in air. This reduction in fatigue life has been attributed to premature crack initiation from surface pits by and higher crack growth rate resulting from synergistic interaction of fatigue and stress corrosion. Although the pitting corrosion behaviour of AA6061 has been studied in depth, its behaviour when simultaneously subjected to a corrosive environment consisting of simulated sea water (or a 3.5% NaCl solution) is not well understood. This investigation studied the corrosion behaviour of aluminium 6061 in the T6 temper condition, and determined the corrosion damage due to influence of temperature and concentration of solution (Kalenda, 2011).

1.3 PROBLEM STATEMENT

Pitting corrosion always influences the local strength of ship hull members. Water pollution and global warming problem affect the concentration of chloride and temperature of seawater increase. When concentration of chloride in seawater increases, it directly increase corrosion rate to the marine applications. Formation of passive films on deterioration aluminium alloys is because of the presence of dissolved oxygen, and chloride ion. This will reduce life time of the product and increase liability marine product. Marine application corrodes rapidly when the temperature of seawater increases. The diffusion of chloride ion through the passive film increases at higher seawater's temperature. Therefore, research of pitting corrosion behaviour in aluminium alloy because of temperature and concentration of seawater are highly beneficial for its prevention in future.

1.4 OBJECTIVES

The main objective of this study is to investigate the pitting corrosion behaviour of aluminium alloy in different concentrations of chloride solution and under static conditions at different temperatures.

1.5 SCOPE

The scopes of this project are as follows:

i. The material that used in this project is AA6061-T6 aluminium alloy.
ii. Different temperatures (25 ℃, 35 ℃, 45 ℃, 55 ℃, 65 ℃) and chloride concentrations (3.5, 4.5 and 5.5 wt%) are used in this study.
iii. Microstructure analysis of the specimens by using scanning electron microscope (SEM).
iv. Electrochemical test is performed by using potentiostat/ galvometer instrument.
v. Corrosion rate is analyzed by IV Man software.

1.6 THESIS OUTLINE

This thesis consists of 5 chapters which illustrate the flow work of this project from introduction until end of the conclusion. There are different contents present in each chapter. Reader will be more understand the detail of the project and obtains the output of the project after they read the entire chapters in thesis.

Chapter 1 discusses the background of the study, problem statement, objectives, and the scope of this study.

Chapter 2 contains all the literature reviews of this study. This chapter also discusses some detail of material that used in this study (aluminium alloy). Detail of pitting corrosion is discussed in Chapter 2. Some explanation of microstructure analysis also will be explained in this chapter.

Chapter 3 discusses the summary of the research methodology of this project. The progress of this project is explained.

Chapter 4 contains the results that achieved during the experiment in this study. This chapter also explains the analysis and discussion of the results of experiment.

Chapter 5 discusses the conclusions of the project. This chapter also contains some future recommendation of this study.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter discusses about phenomena of pitting corrosion, material that used in this project – aluminium alloys and parameters of pitting corrosion that react on aluminium alloys. The first topic explains about the mechanism of pitting corrosion. Stages of pitting corrosion will be explained in detail. Based on the chemical reaction, the formation of pitting corrosion on aluminium alloys in seawater is explained. AA6061 aluminium alloys that are used in this study which include its properties and some explanation about the chosen material are presented. Pitting on AA6061-T6 aluminium alloys is influenced by many different parameters, including concentration of seawater and temperature. Explanation of each parameter will be discussed in this chapter.

2.2 PITTING CORROSION

Pitting corrosion is an electrochemical oxidation-reduction (redox) process which occurs within localized holes on the surface of metal coated with a passive film. Many engineering alloys, such as aluminium alloy are useful because passive film, which are tin oxide layers that in neutral, weakly acidic or alkaline aqueous media on the metal surface greatly reduce the rate of corrosion of the alloys (Frankel, 1998). Accelerated dissolution of the underlying metal occurs because passive film susceptible to localized breakdown. Potential, pH and the duration immerse in aqueous environment are the influences that affect the thickness and structure of oxide film (Naseer et.al, 2007). Figure 2.1 shows the microphotograph of piting corrosion on a un-clad 2024 aluminium alloy.

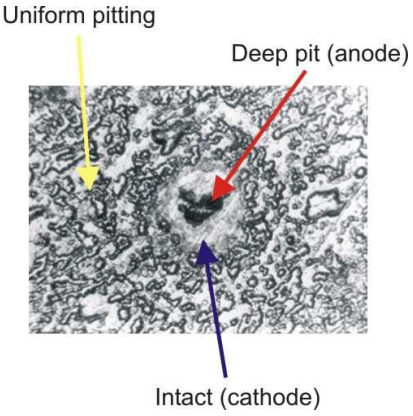

Figure 2.1: Microphotograph of piting corrosion on a un-clad AA2024 aluminium alloy

Source: World's Premier Independent Aviation News Resource

Pitting corrosion is caused by several species such as chloride ions are present in the electrolyte solutions. Normally a pit will occur as a cavity or hole with the surface diameter about some as or less than the depth. Most of the pits develop and grow downward and horizontal surfaces. There are varies of number and shapes in pitting corrosion. Figure 2.2 shows seven typical pit shapes: narrow and deep pits exhibiting crystalline attack, elliptical pit, wide and shallow pits with a polished surface, subsurface/occluded pits growing under a cover constituted of corrosion product or non-corroded metal, undercutting pit, horizontal pit and vertical pit (Ma, 2012).

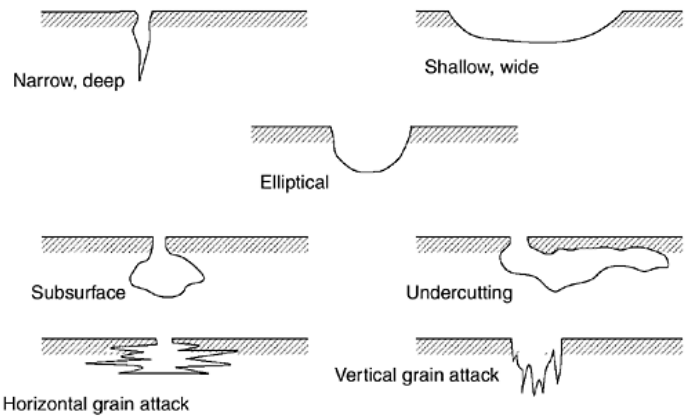

Figure 2.2: Typical pit shapes

Source: Web Corrosion Services

Pitting corrosion is associated with active-passive type alloys and occurs under condition specific to each alloy and environment. Corrosion of pit is a unique type of anodic reaction which is an autocatalytic process in nature. Once a pit starts to grow, the corrosion processes within a pit produce conditions which are both stimulating and necessary for the continuing activity of the pit. This is illustrated schematically in Figure 2.3. The metal is being pitted by an aerated Sodium Chloride (NaCl) solution. The rapid dissolution of metal within the pit tends to produce an excess of positive charge in this area resulting in the migration of chloride ions to maintain electroneutrality, while the oxygen reduction takes place on the adjacent metal surfaces.

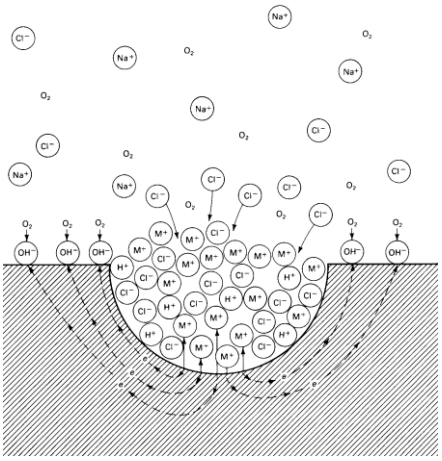

Figure 2.3: Autocatalytic process occurring in a corrosion pit.

Source: U.R.Evans, Corrosion, 7:238 (1951)

Presence of aggressive anion species and chloride ions will affect the formation of passive film breakdown of pitting corrosion (Leckie and Uhlig, 1996). The severity of pitting tends to vary with the logarithm of the bulk chloride concentration. The reason for the aggressiveness of chloride has been pondered for some time, and a number of notions have been put forth.

Consequently, the term concentration cell corrosion has been used to describe the base pitting corrosion. To illustrate the basic mechanism of pitting corrosion, consider a riveted plate section of aluminium alloy immersed in aerated seawater as shown in

Figure 2.3. The overall reaction involves the dissolution of aluminium and the reduction of oxygen to hydroxide ions.

Oxidation: $Al \rightarrow Al^{3+} + 3e^-$ Equation 2.1

Reduction: $O_2 + H_2O + 4e \rightarrow 4OH^-$ Equation 2.2

An oxidation or anodic reaction is indicated by an increase in valence of electron. The local pit environment becomes depletes in cathodic reactant (eg.oxygen), shifts most of the cathodic reaction (such as given by equation 2.1) to boldly exposed surface outside of the pit cavity where this reaction is more plentiful. The pit environment becomes more corrode in metal cations as a result of the dissolution process in the pit grows (Equation 2.3). The concentration of an anodic species such as chloride must increase within the pit in order to maintain charge neutrality by balancing the charge associated with the cation concentration. The positively charged pit attracts negative ions of chlorine Cl^- increasing acidity of the electrolyte according to the reaction:

Overall: $Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+$ Equation 2.3

The pH in the pit is lower (acidity increases) causes acceleration of corrosion process.

As concludion, the local pit environment is reduced in cathodic reactant, such as dissolved oxygen, enriched in metal cation and anionic species (chloride) and acidified. The acidic chloride environment thus generated in pits is aggressive to most metals and tends to propagate the pit growth.

Current density within the pit used to measure the pit penetration rate. The ionic concentration in the pit solution increases when the pit density increases, often reaching supersaturation conditions. Under the alternating current, pitting in aluminium dissolution takes place during the anodic half period, while reduction of protons during the cathodic half period. This will rise in the pH, provoke the formation of a passivating film, resulting in the redistribution of attack. It was obvious from the micrographs (Figure 2.4) that the increase of the current density influenced the graining morphology in the number and the size of the pits. It was also observed by the respective histograms from the image analysis that as the current density increases, the pits population density

(P.P.D.) decreased, while the mean value (M.V.) of the pits size increased (Figure 2.5) (Dimogerontakisa et.al.).

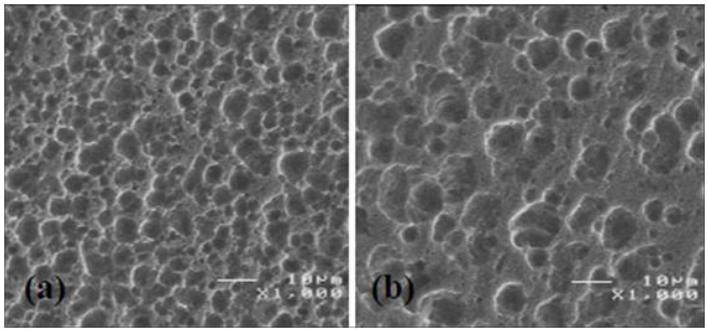

Figure 2.4: SEM micrographs (x1.000) of samples grained with 960 C dm^{-2} at (a) 40 A dm^{-2} and (b) 120 A $dm^{-2.}$

Source: Dimogerontakisa , Campestrinib and Terryna (2006)

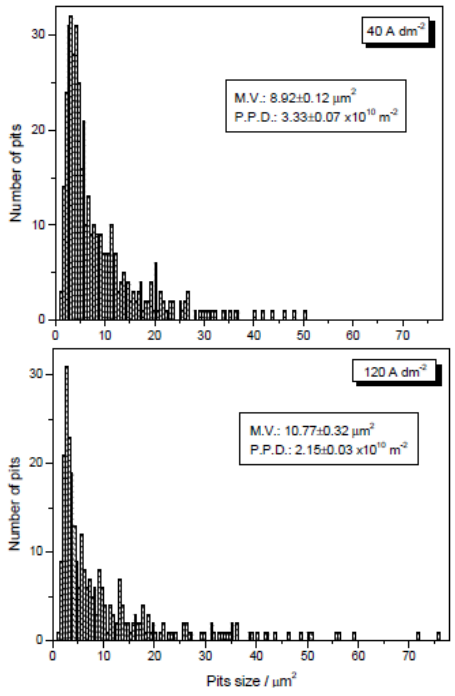

Figure 2.5: Distribution of the pits size for AC-graining with 480 C dm^{-2} at 40 and 120A dm^{-2}

Source: Dimogerontakisa , Campestrinib and Terryna (2006)

2.2.1 Stages of Pitting

Szklarska-Smialowska (1998) states the following four stages of the pitting corrosion process:

i. Process occurring on the passive film;
ii. Process occuring within the passive film, when no visible changes occur in the film;
iii. Formation of so-called metastables pits which initiate and grow below critical pitting potential and then repassivate;
iv. Stable pit growth, above a critical pitting potential.

The initiation and growth of corrosion pit has been, for the purpose of this sub-chapter, divided in 4 steps described (Figure 2.6). Specific examples of pit morphologies representative of the schematic in Figure 2.6 are shown in Figure 2.7.

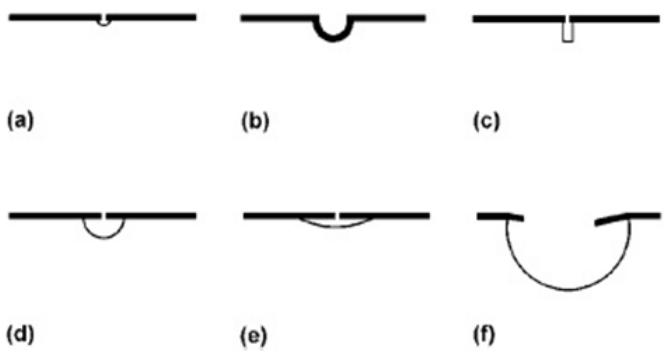

Figure 2.6: Schematic representation of shapes of pit initiation and propagation
Source: Fundamentals of Electrochemical Corrosion

Source: Hewette (1978)

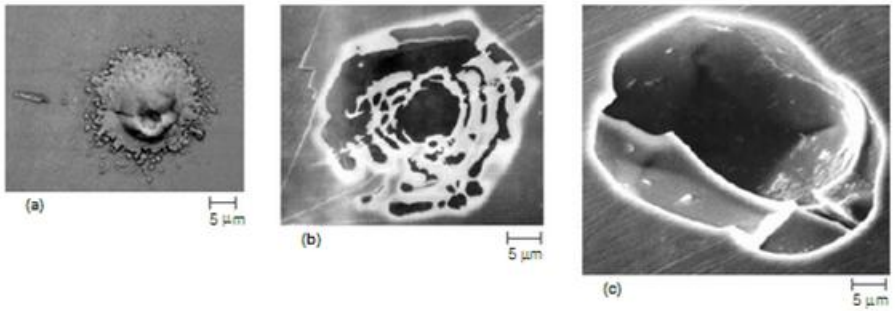

Figure 2.7: Stage of penetration of passive film leading to corrosion pit formation. (a) Initial stage of pit formation. (b) Partially perforated passive film on pit. (c) Fragment of passive film on edge pit.

Source: Hewette (1978)

2.2.1.1 Pit Initiation and Passive Film Breakdown

Breakdown is an occurrence that happens rapidly on a very small scale, making direct observation difficult (Frankel, 1998). Pit initiation and passive film breakdown can be categorized in three type mechanisms which is focus in passive film penetration, film breaking or adsorption (Figure 2.8). The passive film changes in a range of composition, structure, thickness and protectiveness depend on alloy composition, potential, environment, and exposure history (Frankel, 1998). Passive layer form on the reactive metals will increase until 100V without existing of oxygen evolution with thickness reaching several tens of nanometers in thickness to the potential for oxygen evolution. However, the existence of semiconducting properties, valve metals can grow up to a few nanometers in thickness to the potential for oxygen evolution. Figure 2.8 (a) shows the penetration mechanisms for pit initiation where a potential drop at the metal oxide and the oxide-electrolyte interface in these films as well as within the passive layer (Strehblow and Marcus, 1995). In order to initiate pitting corrosion, the aggressive ions migrate into the passive film with penetration method and take place to bring the metal in contact with the aggressive ions solution (Figure 2.8 (b). The adsorption mechanism starts with migration of aggressive anion which is simulated by high electric field in the film. Pitting starts to react when high current circulate through the contaminated zone (Alvarez and Galvele, 2010). Pitting initiation by a film breaking